Novel multiscale framework for modelling of liquid battery electrolytes

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Transport properties of liquid battery electrolytes are conventionally modelled using variants of the Nernst-Planck equation, typically resolving single cationic and anionic species, respectively, hence assuming no ion-pairing, *i.e.* full cation solvation and also vehicular transport in stable solvation shells. Such modelling can straightforwardly use input obtained by electrochemical methods.

There are, however, several emerging classes of electrolytes that render these models inadequate, mainly due to a wider variation in electrolyte composition and charge carriers. As one example, for Li-S battery electrolytes the transport and solvation dynamics of polysulfides are crucial for the cell operation [1]. Another example is highly concentrated electrolytes, where too few solvent molecules are available to fully solvate the cation, leading to complex structure and dynamics by many partially solvated ionic aggregates [2].

To address the transport within such electrolytes, we here propose a novel multiscale method for modelling liquid electrolytes, starting from first principles. The method is based on three consecutive steps building from the microscopic to the mesoscopic: i) A system-specific classical force field is optimized using machine learning algorithms, overcoming problems of conventional force fields [3], while avoiding expensive polarization modelling and with reference data provided by density functional theory calculations, ii) molecular dynamics simulations for nanoseconds to microseconds and systems of 10^4-10^5 atoms provide statistics for, iii) trajectory analysis in a hierarchical manner by identifying clusters of ions and molecules and their structure, transport, and solvation and population dynamics.

The method predicts the structures to be included in continuum models, whose outputs can be directly validated against macroscopic quantities such as ionic conductivity, viscosity and density. Through its multiscale nature, this model yields not only macroscopic predictions, but also insights into how the macroscopic properties emerge from smaller scales.

References:

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